Quantum Theory of Electrical Transport Phenomena. II*

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In a previous paper we have developed a theory of electrical transport phenomena for a simple quantum-mechanical model. That treatment was based on an expansion in powers of the strength of the scattering mechanism. In the present paper we consider the same model, but obtain the transport equation in powers of the *density* of scatterers without restricting ourselves to weak scattering potentials. The expansion involves scattering operators for single centers, pairs of centers, etc., in a manner in many ways analogous to the virial expansion of equilibrium properties. The lowest order terms yield the usual Boltzmann equation. The first correction, in density, to this equation is explicitly given. For the case of spherically symmetric scatterers the solutions of these equations are also obtained.

I. INTRODUCTION

IN a recent paper[1] we have given a theory of the transport equation which describes electrical conductivity for a simplified but physical model of a real substance. The model is as follows. We have a closed system with particles, say electrons, which can carry a current. These electrons are treated as free and independent except for their interaction with an external electric field, and with a collection of fixed but randomly located impurities. By assuming that the interaction between the electrons and impurity centers was weak, we were able to show that to the lowest order in perturbation theory the diagonal matrix elements[2] of the density matrix satisfy the usual Boltzmann equation. (The off-diagonal elements were expressed in terms of the diagonal ones.) In higher orders it was found that the usual Boltzmann equation was *not* valid, and the corrections were calculated up to λ^4, where λ is some dimensionless measure of the strength of the interaction of the impurities with the electrons. As was already noted in I, however, all the correction terms were at least of one order smaller in the density of scattering centers than the "Boltzmann terms," so that in the *low-density limit* the usual Boltzmann equation recovered its validity.

It is the first purpose of this paper to establish this result independently of perturbation theory on the potential. In doing this, we shall set up a general method of approach which enables us to obtain (in principle at least) the transport equation to any desired power of n, the density of scatterers. To illustrate the method in detail, the first-order terms in n (which yield the usual Boltzmann equation), and the second-order terms are computed. The latter are already so complicated that it is probably not feasible to push the method any further.

It should be mentioned at this point what the basic technique is. We have found that it is possible to arrange the solution of the equation for the density matrix in such a way that it involves first the effects of a single scatterer, then of pairs, then triplets, etc., just as in a virial expansion of equilibrium properties. It is then seen that this is a density expansion. The mathematical entities which enter the transport equation are just the "scattering operators"[3] (on and off the energy shell) for an electron on a single center, on a pair of fixed centers, etc. These quantities are assumed known in principle, though of course in practice it may be very difficult to find them exactly, or even to find reasonable approximations to them.

In Sec. II, the general theory of the density expansion is developed. In Sec. III, the "collision" terms (that is the field-independent terms of the transport equation) are calculated to the first and second order in the density. In Sec. IV the "field" terms of the transport equation (that is those terms proportional to the external electric field) are calculated to the zeroth- and first-order in the density. In Sec. V the final transport equation is given to an accuracy which enables us to go one step beyond the lowest order in density. For spherically symmetric scattering centers, the solution is given. Finally in Appendices A, B, and C some of the details not included in the text are treated.

II. GENERAL METHOD

We first recall briefly some of the formulas from I. Let the total density matrix for an ensemble of electrons be ρ_T. Further, let the electric field be turned on at a rate

$$E_\alpha(t)=E_\alpha^0 e^{st}. \tag{1}$$

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[1] W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957). We shall refer to this paper as I in what follows.

[2] That is, diagonal in the representation of plane waves with periodic boundary conditions.

[3] We give only a few of the many references in this field. B. A. Lippman and J. Schwinger, Phys. Rev. **79**, 469 (1950); J. M. Jauch and F. Rohrlich, *Theory of Photons and Electrons* (Addison-Wesley Press, Cambridge, 1955), Chap. 7; K. M. Watson, Phys. Rev. **103**, 489 (1956).

Then we may write

$$\rho_T=\rho+fe^{st}, \tag{2}$$

where ρ is the equilibrium density matrix and f is of the first order in the electric field strength. The matrix f (which we shall often also refer to as the density matrix) satisfies the equation

$$(H,f)-isf=C. \tag{3}$$

Here H is the total Hamiltonian in the absence of the electric field, and C is the commutator

$$C=[\rho,H_1], \tag{4}$$

$$H_1=-eE_\alpha^0 x_\alpha. \tag{5}$$

The Hamiltonian H may be written

$$H=H_0+H', \tag{6}$$

where

$$H_0=p^2/2m, \tag{7}$$

$$H'=\sum_l \varphi(r-r_l), \tag{8}$$

$\varphi(r)$ being the interaction energy of an electron with an impurity center located at the origin and the r_l the locations of the N impurity centers (r and r_l are position *vectors*). Finally, for completeness, we shall give the equilibrium density matrix. Either the Maxwell-Boltzmann or the Fermi-Dirac function may be chosen. For the sake of definiteness we shall think of the Maxwell-Boltzmann distribution (as in I):

$$\rho=Ke^{-\beta H}, \tag{9}$$

$$K^{-1}=\mathrm{Tr}(e^{-\beta H}), \tag{10}$$

but everything goes through just as well for an arbitrary distribution.

Now in I, (3) was solved as follows. It was written in the plane-wave representation (with periodic boundary conditions). The normalized eigenfunctions are

$$\psi_k=(1/\sqrt{\Omega})e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{11}$$

where Ω is the volume of the container. The allowed k_α are given by

$$k_\alpha=(2\pi/L)n_\alpha, \tag{12}$$

where

$$n_\alpha=0,\ \pm1,\ \pm2,\ +3,\ \cdots,\ \pm\infty,$$

and

$$\Omega=L^3.$$

Further

$$H_0\psi_k=\epsilon_k\psi_k, \tag{13}$$

with

$$\epsilon_k=k^2/2m.$$

(Units are again chosen so that $\hbar=1$.)

In this representation it was found that the diagonal and off-diagonal elements of f behaved very differently. The k, k' matrix element ($k\neq k'$) of (3) enabled us to express $f_{kk'}(k\neq k')$ in terms of $f_k(\equiv f_{kk})$, and the diagonal element gave rise to the transport equation for f_k. The process was actually carried out in I as a series in rising powers of λ, i.e., by perturbation theory. We shall now indicate another method which is valid for arbitrarily strong potentials, but which requires an expansion in the density of impurities.

To do this, let us write f as follows

$$f=F+g, \tag{14}$$

where F is the diagonal part of f and g is the off-diagonal part. That is,

$$F_{kk'}=f_k\delta_{kk'}, \tag{15}$$

$$g_{kk'}=f_{kk'}(1-\delta_{kk'}). \tag{16}$$

Substituting in (3) gives

$$[H,g]-isg=[F,H']+isF+C, \tag{17}$$

since F commutes with H_0. Taking matrix elements of this equation, we get

$$([H,g]-isg)_{kk'}=Q_{kk'}, \quad (k\neq k') \tag{18}$$

$$([H,g])_{kk}=isf_k+C_k, \tag{19}$$

where C_k is the diagonal element of C and

$$Q_{kk'}=([F,H'])_{kk'}+C_{kk'}. \quad (k\neq k')$$

In I, (18) was used to express g in terms of F and then (19) became the transport equation.

For purposes of obtaining a *formal* solution of (18) valid for any strength potential it is convenient to rewrite (18) again as an operator equation. To do this, the following definitions prove useful:

$$Q\equiv[F,H']+C', \tag{20}$$

where C' is the nondiagonal part of C, i.e.,

$$C_{kk'}=C_{kk'}(1-\delta_{kk'}). \tag{21}$$

Then, since F is diagonal,

$$Q_{kk}=0. \tag{22}$$

As it stands (18) is satisfied *unless* $k=k'$. We now introduce a matrix G which has the same off-diagonal elements as g, but also suitable diagonal elements. That is, we may write

$$g=G-\Gamma, \tag{23}$$

Γ being the diagonal part of G,

$$\Gamma_{kk'}=G_{kk}\delta_{kk'}. \tag{24}$$

Then (18) gives

$$([H,G-\Gamma]-is(G-\Gamma))_{kk'}=Q_{kk'}, \quad (k\neq k').$$

Or, since Γ is diagonal,

$$([H,G]-isG-[H',\Gamma])_{kk'}=Q_{kk'}, \quad (k\neq k'). \tag{25}$$

The quantity Γ is completely at our disposal, and we choose it so that (25) is valid even if $k=k'$. That is, Γ is determined by

$$([H',G])_{kk}-is\Gamma_k=0,$$

or

$$is\Gamma_k=([H,g])_{kk}, \tag{26}$$

since the diagonal part of G or H cannot contribute to the commutator. Since the choice (26) of Γ makes (25) valid for all k and k', we may write the operator equation

$$[H,G]-isG-(H',\Gamma)=Q. \tag{27}$$

Further, the "transport" Eq. (19) becomes, very simply

$$is\Gamma_k=isf_k+C_k. \tag{28}$$

As in I, f_k is regular for small s, so we may drop isf_k and obtain for our final transport equation

$$is\Gamma_k=C_k. \tag{29}$$

This shows that Γ_k must have, for small s, a $1/s$ singularity if (29) is to be valid as s approaches zero. The explicit calculations below will show this to be the case.

The problem has then been reduced to finding the diagonal matrix element of the solution of the operator Eq. (27).

Now the advantage of having an operator equation of the form of (27) is that it allows for a simple *formal* solution valid for all interaction strengths. This formal solution will then be expanded in powers of the density.

We may write (27) as

$$[H,G]-isG=\Lambda, \tag{30}$$

where

$$\Lambda=Q+[H',\Gamma]. \tag{31}$$

If we regard Λ as known, Eq. (30) is satisfied by the following expression

$$G=\frac{i}{2\pi}\int_{-\infty}^{\infty}R^+(E)\Lambda R^-(E)dE. \tag{32}$$

In this expression

$$R^{\pm}(E)=1/(E-H\pm i\epsilon), \tag{33}$$

with

$$\epsilon=s/2 \tag{34}$$

is the well-known *resolvent* or *Greens function* operator for our problem. It is often convenient to define an operator $R(z)$ where z is a general complex variable by

$$R(z)=1/(z-H). \tag{35}$$

Then

$$R^+(E)=R(E+i\epsilon),\quad R^-(E)=R(E-i\epsilon). \tag{36}$$

From the Hermiticity of H it follows that

$$R^\dagger(z)=R(z^*), \tag{37}$$

where the dagger means Hermitian conjugate. Therefore

$$(R^-)^\dagger=R^+. \tag{38}$$

Multiplying both sides of (35) by $(z-H)$ on the left or on the right, we obtain at once the operator identities

$$\begin{aligned}R(z)&=\frac{1}{d(z)}+\frac{1}{d(z)}H'R(z),\\ R(z)&=\frac{1}{d(z)}+R(z)H'\frac{1}{d(z)},\end{aligned} \tag{39}$$

where

$$d(z)=z-H_0. \tag{40}$$

These identities will prove useful in what follows.

The expression (32) for G is most easily verified in the representation which makes H diagonal. In this representation

$$H\psi_\mu=\epsilon_\mu\psi_\mu. \tag{41}$$

Using (41), (30) yields at once

$$G_{\mu\mu'}=\Lambda_{\mu\mu'}/(\epsilon_\mu-\epsilon_{\mu'}-is). \tag{42}$$

On the other hand, (32) gives

$$G_{\mu\mu'}=\frac{i}{2\pi}\int_{-\infty}^{\infty}dE\frac{1}{E-\epsilon_\mu+i\epsilon}\frac{1}{E-\epsilon_{\mu'}-i\epsilon}\Lambda_{\mu\mu'}.$$

Carrying out the indicated integration (by closing the contour in the lower half of the E plane, for example), we obtain (42) again, so that (32) is really the solution of (30).

We note next that (27) is a linear equation for G. That means that if Q consists of two parts,

$$Q=Q^{(1)}+Q^{(2)},$$

then

$$G=G^{(1)}+G^{(2)},\quad \Gamma=\Gamma^{(1)}+\Gamma^{(2)}, \tag{43}$$

$\Gamma^{(1)}$ and $\Gamma^{(2)}$ being the diagonal parts of $G^{(1)}$ and $G^{(2)}$, respectively. $G^{(1)}$ and $G^{(2)}$ satisfy

$$[H,G^{(1)}]-isG^{(1)}-(H',\Gamma^{(1)})=Q^{(1)}, \tag{44}$$

$$[H,G^{(2)}]-isG^{(2)}-(H',\Gamma^{(2)})=Q^{(2)}. \tag{45}$$

For our case we take

$$\begin{aligned}Q^{(1)}&=[F,H'],\\ Q^{(2)}&=C'.\end{aligned} \tag{46}$$

We shall consider $G^{(1)}$ first. Equation (32) gives

$$G^{(1)}=\frac{i}{2\pi}\int_{-\infty}^{\infty}R^+[U,H']R^-dE, \tag{47}$$

where

$$U=F-\Gamma^{(1)}. \tag{48}$$

U is diagonal in the k representation.

We next introduce—*exitus acta probat*—in place of R the *scattering operator* T. In terms of T, (47) will simplify considerably. The scattering operator is defined formally as follows.

$$T(z)=d(z)R(z)d(z)-d(z),$$

or

$$R(z)=\frac{1}{d(z)}+\frac{1}{d(z)}T(z)\frac{1}{d(z)}. \tag{49}$$

If H' were a localized scattering potential, the limit $T_{kk'}(\epsilon_k+i\epsilon)$, as $\epsilon\to 0$, would fully determine the scattering.[4] For the present, however, we shall only need some formal properties of $T(z)$.

From (37), we have at once that

$$T^\dagger(z)=T(z^*). \tag{50}$$

Further, inserting (49) in (39), we obtain the identities

$$T=H'\left(1+\frac{1}{d}T\right),\quad T=\left(1+T\frac{1}{d}\right)H'. \tag{51}$$

(The variable z or E will often not be written explicitly.) Finally, it is convenient to introduce $T^{\pm}(E)$ defined by

$$T^{\pm}(E)=T(E\pm i\epsilon). \tag{52}$$

Now inserting (49) in (47) and making use of (51), we have

$$G^{(1)}=\frac{i}{2\pi}\int_{-\infty}^{\infty}dE\left\{U\frac{1}{d^+}T^-\frac{1}{d^-}-\frac{1}{d^+}T^+\frac{1}{d^-}U-2i\epsilon\frac{1}{d^+}T^+\frac{U}{d^+d^-}T^-\frac{1}{d^-}\right\}, \tag{53}$$

where we have also used the fact that U commutes with d. Taking diagonal matrix elements of (53), we obtain

$$\Gamma_k{}^{(1)}=\frac{i}{2\pi}\int_{-\infty}^{\infty}\frac{dE}{d_k{}^+d_k{}^-}\left\{U_k(T_{kk}{}^--T_{kk}{}^+)-2i\epsilon\sum_{k'}\frac{T_{kk'}{}^+T_{k'k}{}^-U_{k'}}{|d_{k'}{}^+|^2}\right\}. \tag{54}$$

Now $T_{kk}{}^+(E)$ regarded as a function of the complex variable E is regular in the upper half-plane,[5] the singularities of T [from (49)] being the same as those of R. (Those of R are found most easily in the representation (41) where we have an explicit expression for R.) Similarly $T_{kk}{}^-(E)$ is regular in the lower half of the E plane. Therefore we have

$$\int_{-\infty}^{\infty}dE\frac{T_{kk}{}^+}{d_k{}^+d_k{}^+}=0=\int_{-\infty}^{\infty}dE\frac{T_{kk}{}^-}{d_k{}^-d_k{}^-}, \tag{55}$$

since in one case we can close the contour in the upper half plane and enclose no singularities while in the other we can close in the lower half plane. We can now rewrite (54) as

$$\Gamma_k{}^{(1)}=\frac{i}{2\pi}\int_{-\infty}^{\infty}dE\left\{U_k\left[T_{kk}{}^-\left\{\frac{1}{d_k{}^+d_k{}^-}-\frac{1}{d_k{}^-d_k{}^-}\right\}-T_{kk}{}^+\left\{\frac{1}{d_k{}^+d_k{}^-}-\frac{1}{d_k{}^+d_k{}^+}\right\}\right]-2i\epsilon\sum_{k'}\frac{T_{kk'}{}^+T_{k'k}{}^-U_{k'}}{|d_{k'}{}^+|^2|d_k{}^+|^2}\right\}$$

$$=\frac{\epsilon}{\pi}\int_{-\infty}^{\infty}\frac{dE}{|d_k{}^+|^2}\left\{U_k\left[\frac{T_{kk}{}^-}{d_k{}^-}+\frac{T_{kk}{}^+}{d_k{}^+}\right]+\sum_{k'}\frac{T_{kk'}{}^+T_{k'k}{}^-U_{k'}}{|d_{k'}{}^+|^2}\right\}. \tag{56}$$

The final simplification comes from the identity

$$1=\frac{\epsilon}{\pi}\int_{-\infty}^{\infty}R^+R^-dE, \tag{57}$$

which is most easily seen by doing the integration in the representation (41), or by using (32) for the special $\Lambda=1$. Inserting (49) in (57) and taking the diagonal element, we have

$$1=\frac{\epsilon}{\pi}\int_{-\infty}^{\infty}\frac{dE}{|d_k{}^+|^2}\left\{1+\frac{T_{kk}{}^-}{d_k{}^-}+\frac{T_{kk}{}^+}{d_k{}^+}+\sum_{k'}\frac{T_{kk'}{}^+T_{k'k}{}^-}{|d_{k'}{}^+|^2}\right\}. \tag{58}$$

The first integral may be performed at once, giving π/ϵ, so that (58) becomes

$$0=\frac{\epsilon}{\pi}\int_{-\infty}^{\infty}\frac{dE}{|d_k{}^+|^2}\left\{\frac{T_{kk}{}^-}{d_k{}^-}+\frac{T_{kk}{}^+}{d_k{}^+}+\sum_{k'}\frac{T_{kk'}{}^+T_{k'k}{}^-}{|d_{k'}{}^+|^2}\right\}. \tag{59}$$

(This result is very closely related to the well-known *optical theorem* of ordinary scattering theory, and will be investigated further in Appendix C.) Multiplying (59) by U_k and subtracting from (56), we obtain our final result for $\Gamma_k{}^{(1)}$, i.e.,

$$\Gamma_k{}^{(1)}=\sum_{k'}\frac{\epsilon}{\pi}\int_{-\infty}^{\infty}dE\frac{T_{kk'}{}^+T_{k'k}{}^-}{|d_k{}^+|^2|d_{k'}{}^+|^2}(U_{k'}-U_k),$$

or

$$is\Gamma_k{}^{(1)}=\sum_{k'}J_{kk'}(U_{k'}-U_k)=\sum_{k'}J_{kk'}[(f_{k'}-f_k)-(\Gamma_{k'}{}^{(1)}-\Gamma_k{}^{(1)})], \tag{60}$$

where

$$J_{kk'}=\frac{2i\epsilon^2}{\pi}\int_{-\infty}^{\infty}dE\frac{T_{kk'}{}^+T_{k'k}{}^-}{|d_k{}^+|^2|d_{k'}{}^+|^2}. \tag{61}$$

Equation (60) is not an explicit expression for $\Gamma_k{}^{(1)}$. In fact, if we replace the summation over k' by an integration, (60) becomes an integral equation for $\Gamma_k{}^{(1)}$. However, if we want a density expansion this fact gives us little trouble. Since we anticipate that in the dilute limit the usual Boltzmann equation is valid, we may

[4] See B. A. Lippman and J. Schwinger, reference 3.
[5] See K. M. Watson, reference 3.

conclude [via (29)] that $J_{kk'}$ will have as its lowest order term something *linear* in n (this will be verified below). Therefore Eq. (60) may be made the basis of a systematic iteration procedure in which first $\Gamma_k^{(1)}$ is ignored on the right-hand side of (60). That is, assume we have somehow gotten a density expansion for $J_{kk'}$,

$$J_{kk'}=J_{kk'}^{(1)}+J_{kk'}^{(2)}+\cdots, \tag{62}$$

where $J_{kk'}^{(1)}$ is proportional to n, $J_{kk'}^{(2)}$ to n^2, etc. Further put

$$is\Gamma_k^{(1)}=A_k^{(1)}+A_k^{(2)}+\cdots, \tag{63}$$

where once again $A_k^{(1)}$ is proportional to n, $A_k^{(2)}$ to n^2, etc.

Substituting (62) and (63) in (60), we obtain on equating terms of the same order in n:

$$A_k^{(1)}=\sum_{k'} J_{kk'}^{(1)}(f_{k'}-f_k), \tag{64}$$

$$A_k^{(2)}=\sum_{k'}\left\{J_{kk'}^{(2)}(f_{k'}-f_k)-\frac{1}{2i\epsilon}J_{kk'}^{(1)}(A_{k'}^{(1)}-A_k^{(1)})\right\}, \tag{65}$$

etc.

All that is required is the expansion (62) of $J_{kk'}$. It may be pointed out that (65) seems to imply that $A_k^{(2)}$ gets singular as s or $\epsilon\to 0$. This is only apparent however; we shall see in the detailed calculations given below that the first term of (65) also has a singularity which just compensates this.

We come finally to the crucial part of our entire analysis, the density expansion (62). This is obtained by means of what we shall call the *virial* expansion of the scattering operator T. The derivation of this expansion is given in Appendix A. The result may be stated as follows

$$T=\sum_l Q_l+\frac{1}{2!}\sum_{lm}{}' Q_{lm}+\frac{1}{3!}\sum_{lmn}{}' Q_{lmn}+\cdots, \tag{66}$$

where l, m, n, $\cdots$ are indices labeling the N scattering centers. The prime on the summation means *all* the indices are unequal. The Q's are given by

$$Q_l=T_l, \tag{67}$$

$$Q_{lm}=T_{lm}-(Q_l+Q_m)=T_{lm}-T_l-T_m, \tag{68}$$

$$Q_{lmn}=T_{lmn}-(Q_{lm}+Q_{mn}+Q_{nl}+Q_l+Q_m+Q_n)=T_{lmn}-T_{lm}-T_{mn}-T_{nl}+T_l+T_m+T_n, \tag{69}$$

etc.

The T_l, T_{lm}, etc. are the scattering operators if only the center at $\mathbf{r}_l$ is present, if only those at $\mathbf{r}_l$, $\mathbf{r}_m$ are present, etc., respectively. (See Appendix A for the formal definitions.)

The expression (66) is an identity. We have however arranged things so that the first term refers to properties of a *single* center, the next to those of any *two* centers, etc. As in the theory of equilibrium properties this type of arrangement gives rise to a density expansion.

We now must substitute (66) in (61). If we do this and again collect those terms which refer to a single center, those which refer to two centers, etc., the result is—after some algebra—again quite simple. Let us put

$$T_{kk'}{}^{+}T_{k'k}{}^{-}=\sum_l X_l+\frac{1}{2!}\sum_{lm}{}' X_{lm}+\frac{1}{3!}\sum_{lmn}{}' X_{lmn}+\cdots. \tag{70}$$

Then we find

$$X_l=(T_l{}^{+})_{kk'}(T_l{}^{-})_{k'k}=|(T_l{}^{+})_{kk'}|^2, \tag{71}$$

$$X_{lm}=(T_{lm}{}^{+})_{kk'}(T_{lm}{}^{-})_{k'k}-(X_l+X_m)=|(T_{lm}{}^{+})_{kk'}|^2-|(T_l{}^{+})_{kk'}|^2-|(T_m{}^{+})_{kk'}|^2, \tag{72}$$

$$X_{lmn}=|(T_{lmn}{}^{+})_{kk'}|^2-(X_{lm}+X_{mn}+X_{nl}+X_l+X_m+X_n), \tag{73}$$

and so forth.

As we shall see, the decomposition (70) gives rise in fact to a density expansion. Anticipating this we may write

$$J_{kk'}^{(1)}=\frac{2i\epsilon^2}{\pi}\int_{-\infty}^{\infty}dE\frac{\sum_l|(T_l{}^{+})_{kk'}|^2}{|d_k{}^{+}|^2|d_{k'}{}^{+}|^2}, \tag{74}$$

$$J_{kk'}^{(2)}=\frac{i\epsilon^2}{\pi}\int_{-\infty}^{\infty}\frac{\sum_{lm}[|(T_{lm}{}^{+})_{k'}|^2-|(T_l{}^{+})_{kk'}|^2-|(T_m{}^{+})_{kk'}|^2]}{|d_k{}^{+}|^2|d_{k'}{}^{+}|^2}, \tag{75}$$

etc. The evaluation of these expressions up to and including $J_{kk'}^{(2)}$ will be carried out in Sec. III, and by means of them $\Gamma_k^{(1)}$ will be obtained to the second order in n.

To complete the discussion of the left-hand side of the transport Eq. (29), we need $\Gamma_k^{(2)}$. From (45), (46), and (32) we have

$$\Gamma_k^{(2)}=\frac{i}{2\pi}\int_{-\infty}^{\infty}dE[R^{+}(C'-(\Gamma^{(2)},H'))R^{-}]_{kk}. \tag{76}$$

The second term in the integrand may be treated by the identical procedures that led from (47) to (61), so that

$$is\Gamma_k^{(2)}=-\frac{\epsilon}{\pi}\int_{-\infty}^{\infty}dE(R^{+}C'R^{-})_{kk}-\sum_{k'}J_{kk'}(\Gamma_{k'}^{(2)}-\Gamma_k^{(2)}). \tag{77}$$

Again, let us put

$$is\Gamma_k^{(2)}=B_k^{(1)}+B_k^{(2)}+\cdots, \tag{78}$$

$B_k^{(1)}$ being linear in the density, $B_k^{(2)}$ quadratic, etc. Then, just as in the discussion following (60), since $J_{kk'}$ starts with terms linear in n, to the lowest order in n the last term of (77) may be ignored. This can be made, exactly as before, part of a systematic expansion in powers of n. Therefore it only remains to obtain a density expansion for the first term on the right-hand side of (77).

Let us write, using (49),

$$\int_{-\infty}^{\infty} dE(R^+C'R^-)_{kk}$$

$$=\int_{-\infty}^{\infty} dE\frac{1}{|d_k^+|^2}\Big[\sum_{k'}\Big(\frac{T_{kk'}^+(C')_{kk'}}{d_{k'}^+}+\frac{(C')_{k'k}T_{k'k}^-}{d_{k'}^-}\Big)$$

$$+\sum_{k',k''}T_{kk'}^+\frac{(C')_{kk'}}{d_{k'}^+ d_{k''}^-}T_{k''k}^-\Big], \quad (79)$$

since $(C')_{kk}=0$.

We now make once again a "virial" expansion for the integrand. This is done by using (66) and noting from Appendix B [Eq. (B7)] that we may write

$$C'=\sum_l (C')_m+\frac{1}{2!}\sum_{lm}' (C')_{lm}+\cdots.$$

Inserting these in (79) and collecting together terms which refer to only a single center, those which refer to two distinct centers, etc., we obtain a series of the form

$$-\frac{\epsilon}{\pi}\int_{-\infty}^{\infty} dE(R^+C'R^-)_{kk}=\sum_l Y_l+\frac{1}{2!}\sum_{lm}' Y_{lm}+\cdots, \quad (80)$$

where

$$Y_l=-\frac{\epsilon}{\pi}\int_{-\infty}^{\infty}\frac{dE}{|d_k^+|^2}$$

$$\times\sum_l\Big[\sum_{k'}\Big(\frac{(T_l^+)_{kk'}(C_l')_{k'k}}{d_{k'}^+}+\frac{(C_l')_{kk'}(T_l^-)_{k'k}}{d_{k'}^-}\Big)$$

$$+\sum_{k',k''}\frac{(T_l^+)_{kk'}(C_l')_{k'k''}(T_l^-)_{k''k}}{d_{k'}^+ d_{k''}^-}\Big]. \quad (81)$$

The higher order terms are not difficult to write down, but they are very unwieldly. For our purposes, the leading term (81) will be sufficient. As we shall see, the decomposition (80) gives rise to a density expansion, so that

$$B_k^{(1)}=+\sum_l Y_m. \quad (82)$$

To summarize the results of this section we may say that the left-hand side of the "transport equation" (29) can be expanded in powers of the density

$$is\Gamma_k=A_k^{(1)}+A_k^{(2)}+\cdots+B_k^{(1)}+B_k^{(2)}+\cdots, \quad (83)$$

$A_k^{(1)}$ and $A_k^{(2)}$ being obtained from (64) and (65), $B_k^{(1)}$ from (82).

The A terms in (29) are linear in the distribution function f_k, and we shall refer to them as the "collision" terms. The B terms and the commutator C_k are linear in the electric field, and we shall call them the "field" terms. The transport equation then has the form

$$\mathfrak{L}_k F=eE_\alpha^0 M_{\alpha k}, \quad (84)$$

where $\mathfrak{L}_k F$ is some linear operator acting on the diagonal elements of f, and $M_{\alpha k}$ is some function of k. From all that has gone before, we know that

$$\mathfrak{L}_k=n(\mathfrak{L}_k^{(0)}+\mathfrak{L}_k^{(1)}+\cdots), \quad (85)$$

$$M_{\alpha k}=M_{\alpha k}^{(0)}+M_{\alpha k}^{(1)}+M_{\alpha k}^{(2)}+\cdots, \quad (86)$$

the superscript indicating to which power of n the term is proportional. It therefore follows that, if we expand F in n, its first term is $O(1/n)$ and we may write

$$F=(1/n)(F^{(0)}+F^{(1)}+\cdots). \quad (87)$$

Substituting (85), (86), and (87) in (84) and equating equal powers of n, we obtain

$$\mathfrak{L}_k^{(0)}F^{(0)}=eE_\alpha^0 M_{\alpha k}^0, \quad (88)$$

$$\mathfrak{L}_k^0 F^{(1)}+\mathfrak{L}_k^{(1)}F^{(0)}=eE_\alpha^0 M_{\alpha k}^{(1)}, \quad (89)$$

etc.

Equation (88) is the lowest order transport equation. It requires a knowledge of the collision terms to the first order in n, and the field terms to the zeroth order. As we shall see in Sec. V, this is the ordinary Boltzmann equation. Equation (89) enables us to calculate the first correction to $F^{(0)}$. It requires knowledge of the collision terms to n^2 and of the field terms to n. The main labor of this paper lies in the calculation of the relevant quantities entering into (89).

III. CALCULATION OF THE COLLISION TERMS

To obtain the collision terms to $O(n^2)$, we need $J_{kk'}^{(1)}$ and $J_{kk'}^{(2)}$, as given by (74) and (75), from which $A_k^{(1)}$ and $A_k^{(2)}$ may be calculated from (64) and (65). Because of the presence of the $1/\epsilon$ in (65), knowledge of $J_{kk'}^{(1)}$ is required up to and including terms linear in ϵ. We begin with $J_{kk'}^{(1)}$. By Eq. (C4) of Appendix C

$$(T_l^+)_{kk'}=e^{-i(k-k')\cdot r_l}t_{kk'}^+, \quad (90)$$

where t^+ is the scattering operator for a single scatterer located at the origin. Equation (74) then becomes

$$J_{kk'}^{(1)}=N\frac{2i\epsilon^2}{\pi}\int_{-\infty}^{\infty} dE\frac{|t_{kk'}^+(E)|^2}{|d_k^+|^2|d_{k'}^+|^2}$$

$$=N\frac{2i\epsilon^2}{\pi}\int_{-\infty}^{\infty} dE\frac{t_{kk'}^+(E)t_{k'k}^-(E)}{(E-\epsilon_k+i\epsilon)(E-\epsilon_{k'}+i\epsilon)(E-\epsilon_k-i\epsilon)(E-\epsilon_{k'}-i\epsilon)}. \quad (91)$$

We can evaluate the integral in (91) most easily by contour integration. The integrand has, in the complex E plane, the following singularities (Appendix C): simple poles at $E=\epsilon_b\pm i\epsilon$, $\epsilon_k\pm i\epsilon$, $\epsilon_{k'}\pm i\epsilon$; branch cuts starting at $\pm i\epsilon$ and extending to $+\infty$ parallel to the real axis. Now since we are integrating along the real axis, the value of the integrand is not changed if we move the branch cuts in any way which does not make them cross the real axis. This is convenient to do because the poles of the integrand now no longer lie on the branch cuts. The situation is given in Fig. 1, where the branch lines have been rotated to the imaginary axis. By deforming the path of integration, we may now write

$$\int_{-\infty}^{\infty}=\int_{\gamma_1}+\int_{\gamma_2}+\int_{\gamma_3}+\int_{\gamma_4}. \tag{92}$$

The integral around the branch cut (γ_4) is the most difficult to evaluate. However, the integrand on γ_4 is perfectly regular (ϵ_k and $\epsilon_{k'}$ are fixed and assumed not zero) as $\epsilon\to 0$ so that the result is independent of ϵ. However, $J_{kk'}{}^{(1)}$ contains an extra factor of ϵ^2 [from (91)], so that the error in neglecting γ_4 is $O(\epsilon^2)$. To the order (in n) which we are considering, we only need $J_{kk'}{}^{(1)}$ to $O(\epsilon)$, so that it is permissible to drop the γ_4 integral. Evaluating the γ_1, γ_2, and γ_3 integrals by residues we have

$$J_{kk'}{}^{(1)}=2i\epsilon N\Big\{\sum_b|(k|b)|^2|(k'|b)|^2 + \frac{t_{kk'}(\epsilon_{k'}{}^+)t_{k'k}(\epsilon_{k'}-is)}{x(x-is)} + \frac{t_{kk'}(\epsilon_{k'}{}^+)t_{k'k}(\epsilon_{k'}-is)}{x(x+is)}\Big\}, \tag{93}$$

where $(k|b)$ is the Fourier transform of the bound state function ψ_b associated with a single center [see Appendix C, (C20), (C23)]. Further, $x=\omega_{kk'}=\epsilon_k-\epsilon_{k'}$, and

$$t_{kk'}(\epsilon_k{}^+)=\lim_{\eta\to 0^+}t_{kk'}(\epsilon_k+i\eta). \tag{94}$$

The form (93) which arises out of the contour integration is unsymmetric, and it is convenient for later purposes to transform it somewhat.

Writing

$$\begin{aligned}&t_{kk'}(\epsilon_k{}^+)t_{k'k}(\epsilon_k-is)\\&=\lim_{\eta\to 0^+}t_{kk'}(\epsilon_k+i\epsilon+i\eta-i\epsilon)t_{k'k}(\epsilon_k-i\epsilon-i\epsilon)\\&=t_{kk'}{}^+(\epsilon_k)t_{k'k}{}^-(\epsilon_k) -i\epsilon\left[\frac{\partial|t_{kk'}{}^+(E)|^2}{\partial E}\right]_{E=\epsilon_k}+O(\epsilon^2),\end{aligned} \tag{95}$$

Eq. (93) becomes

$$J_{kk'}{}^{(1)}=2i\epsilon N\Big\{\sum_b|(k|b)|^2|(k'|b)|^2 + \frac{|t_{kk'}{}^+(\epsilon_k)|^2}{x(x-is)}+\frac{|t_{kk'}{}^+(\epsilon_{k'})|^2}{x(x+is)}\Big\} -i\epsilon\Big[\frac{[\partial|t_{kk'}{}^+(E)|^2/\partial E]_{E=\epsilon_k}}{x(x-is)} + \frac{[\partial|t_{kk'}{}^+(E)|^2/\partial E]_{E=\epsilon_{k'}}}{x(x+is)}\Big]. \tag{96}$$

Writing

$$\frac{1}{x-is}=\frac{x}{x^2+s^2}+i\frac{s}{x^2+s^2},$$

Eq. (96) becomes

$$J_{kk'}{}^{(1)}=iN\Big\{s\sum_b|(k|b)|^2|(k'|b)|^2 + \frac{s}{x^2+s^2}(|t_{kk'}{}^+(\epsilon_k)|^2+|t_{kk'}{}^+(\epsilon_{k'})|^2) + is\frac{1}{x^2+s^2}\Big[\frac{|t_{kk'}{}^+(\epsilon_k)|^2-|t_{kk'}{}^+(\epsilon_{k'})|^2}{x} - \frac{[\partial|t_{kk'}{}^+(E)|^2/\partial E]_{\epsilon_k}+[\partial|t_{kk'}{}^+(E)|^2/\partial E]_{\epsilon_{k'}}}{2}\Big]\Big\}. \tag{97}$$

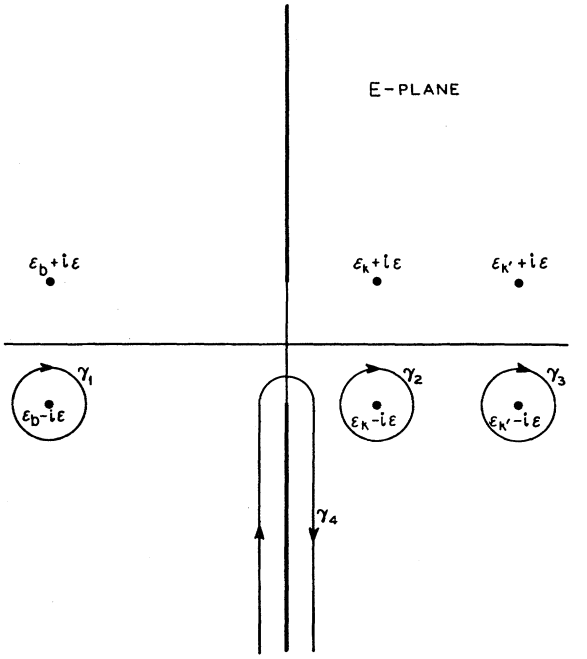

FIG. 1. Contours for the evaluation of (91). The heavy dots represent poles and the heavy lines branch cuts.

In (97) we have again dropped a term of the order of s^2. In the limit of $s\to 0$, we have

$$s/(x^2+s^2)=\pi\delta(x). \tag{98}$$

We can take this limit for the last two terms of (97) since they are already of the order of s. Doing this, and noticing that

$$\lim_{\epsilon_{k'}\to\epsilon_k}\frac{|t_{kk'}{}^+(\epsilon_k)|^2-|t_{kk'}{}^+(\epsilon_{k'})|^2}{x}=\left\{\frac{\partial|t_{kk'}{}^+(E)|^2}{\partial E}\right\}_{\epsilon_k}, \tag{99}$$

we see that the entire square bracket in (97) cancels, leaving us with

$$J_{kk'}{}^{(1)}=iN\left\{s\sum_b|(k|b)|^2|(k'|b)|^2+\frac{s}{x^2+s^2}\times(|t_{kk'}{}^+(\epsilon_k)|^2+|t_{kk'}{}^+(\epsilon_{k'})|^2\right\}\equiv iN\sigma_{kk'}. \tag{100}$$

Since t is proportional to $1/\Omega$ and $(k|b)$ to $1/\sqrt{\Omega}$, the dependence of $J_{kk'}{}^{(1)}$ on the size of the system goes as n/Ω. If the summation in (64) is replaced by an integration we have another factor of $\Omega/(2\pi)^3$, so that $J_{kk'}{}^{(1)}$ gives rise to an integral operator which is proportional to n. This checks the assumption made in discussing (84). The leading term of $J_{kk'}{}^{(1)}$ is obtained by letting $s\to 0$ and is, by (98),

$$J_{kk'}{}^{(1)}=iN2\pi\delta(\omega_{kk'})|t_{kk'}{}^+(\epsilon_k)|^2+O(s)=iNw_{kk'}+O(s) \tag{101}$$

where $w_{kk'}$ is just the *exact* transition probability per unit time for the scattering of an electron in state k' to the state k by a single scattering center.[4]

Incidently it should be mentioned that this result can be obtained much more simply by noting that

$$\lim_{\epsilon\to 0}\left(\frac{\epsilon}{\pi}\cdot\frac{1}{|d^+|^2}\right)=\delta(E-\epsilon_k). \tag{102}$$

Inserting this in the integral (91) gives (101) at once. The more elaborate derivation given is necessary to obtain the $O(s)$ terms.

From (101) and (64), we have

$$A_k{}^{(1)}=iN\sum_{k'}w_{kk'}(f_{k'}-f_k). \tag{103}$$

In order to calculate $A_k{}^{(2)}$ we need $J_{kk'}{}^{(2)}$. By (65) we need it only up to the zeroth order in ϵ. (There will be terms in $1/\epsilon$ which of course we must retain.) $J_{kk'}{}^{(2)}$ is given by (75). Unlike (74), (75) depends on the positions of the scatterers. However, just as in I, it can be shown that for a sufficiently large volume (75) may be replaced by its *ensemble average*, i.e., its average over all possible positions of the scatterers. Thus, we may put

$$J_{kk'}{}^{(2)}=\frac{i\epsilon^2}{\pi}\int_{-\infty}^{\infty}dE\frac{\sum_{lm}{}'[\langle|(T_{lm}{}^+)_{kk'}|^2\rangle-\langle|(T_l{}^+)_{kk'}|^2\rangle-\langle|(\Gamma_m{}^+)_{kk'}|^2\rangle]}{|d_k{}^+|^2|d_{k'}{}^+|^2}, \tag{104}$$

where the symbol $\langle\ \rangle$ indicates the ensemble average. [See I, Eq. (37).]

The detailed justification of (104) is quite straightforward. Making use of the results of Appendix C [(C4) and the multiple scattering expansion (C12)], we see that each term of (104) gives rise to a term in (75) of exactly the same form as the terms of I, Appendix B, Eq. (B1), for which we have already justified the use of the ensemble average.

Since the ensemble average for any pair lm is the same, we may write

$$J_{kk'}{}^{(2)}=N(N-1)\frac{i\epsilon^2}{\pi}\int_{-\infty}^{\infty}dE\times\frac{\langle|(T_{lm}{}^+)_{kk'}|^2\rangle-\langle|(T_l{}^+)_{kk'}|^2\rangle-\langle|(T_m{}^+)_{kk'}|^2\rangle}{|d_k{}^+|^2|d_{k'}{}^+|^2}. \tag{105}$$

It is difficult to go much further without some knowledge of the two-center scattering operator $T_{lm}{}^+(E)$. The reason for this is that in order to do the integral (105) we need to know the nature of the functional dependence of the integrand on E, after the ensemble averaging. This is best obtained by again making use of the multiple scattering expansion[6] (C12), which gives

$$\begin{aligned}&|(T_{lm}{}^+)_{kk'}|^2-|(T_l{}^+)_{kk'}|^2-|(T_m{}^+)_{kk'}|^2\\&=\Bigg[(T_l{}^+)_{kk'}(T_m{}^-)_{k'k}+\sum_{k_1}\Bigg\{\frac{(T_l{}^+)_{kk'}(T_l{}^-)_{k'k_1}(T_m{}^-)_{k_1k}}{d_{k_1}{}^-}\\&\quad+\frac{(T_l{}^+)_{kk'}(T_m{}^-)_{k'k_1}(T_l{}^-)_{k_1k}}{d_{k_1}{}^-}\\&\quad+\frac{(T_l{}^+)_{kk_1}(T_m{}^+)_{k_1k'}(T_l{}^-)_{k'k}}{d_{k_1}{}^+}\\&\quad+\frac{(T_l{}^+)_{kk_1}(T_m{}^+)_{k_1k'}(T_m{}^-)_{k'k}}{d_{k_1}{}^+}\Bigg\}\\&\quad+\sum_{k_1,\,k_2}\frac{(T_l{}^+)_{kk_1}(T_m{}^+)_{k_1k'}(T_m{}^-)_{k'k_2}(T_l{}^-)_{k_2k}}{d_{k_1}{}^+d_{k_2}{}^-}\\&\qquad+(l\leftrightarrow m)\Bigg]+L_{kk'}.\end{aligned} \tag{106}$$

[6] In the neighborhood of a bound state (where t has a simple pole) the multiple scattering series will certainly be invalid since higher and higher powers of t enter. However, just as in the discussion of $J_{kk'}{}^{(1)}$, we see that the bound states of T_{lm} and t only

Here we have written the first few terms down explicitly, and have indicated the remainder by $L_{kk'}$. The meaning of this decomposition is the following: the terms $L_{kk'}$ have an ensemble average which is a smooth function of E, and which tend to a well-defined limit as $\epsilon\to 0$.[7]

We would like to emphasize the fact that the calculation of the ensemble average of $L_{kk'}$ requires only a knowledge of the usual scattering operators, that is, T_{lm}, T_l, T_m in the limit of *infinite* volume. To see this, we imagine $L_{kk'}$ expressed in terms of the (finite volume) scattering operators by (106). It may then be verified from the explicit expansion of T_{lm} that in this expression one may pass to the limit of infinite volume without affecting the ensemble average of $L_{kk'}$. Substituting (106) in (105), we obtain

$$J_{kk'}{}^{(2)}=iN^2(I_{kk'}{}^{(0)}+I_{kk'}{}^{(1)}+I_{kk'}{}^{(1)*}+I_{kk'}{}^{(2)}+I_{kk'}{}^{(2)*}+I_{kk'}{}^{(3)}), \quad (107)$$

where

$$I_{kk'}{}^{(0)}=\frac{\epsilon^2}{\pi}\int_{-\infty}^{\infty}dE\frac{\langle L_{kk'}(E)\rangle}{|d_k{}^+|^2|d_{k'}{}^+|^2}, \quad (108)$$

$$I_{kk'}{}^{(1)}=\frac{2\epsilon^2}{\pi}\int_{-\infty}^{\infty}dE\frac{|t_{kk'}{}^+|^2t_{kk}{}^-}{|d_k{}^+|^2|d_{k'}{}^+|^2d_k{}^-}, \quad (109)$$

$$I_{kk'}{}^{(2)}=\frac{2\epsilon^2}{\pi}\int_{-\infty}^{\infty}dE\frac{|t_{kk'}{}^+|^2t_{k'k'}{}^-}{|d_k{}^+|^2|d_{k'}{}^+|^2d_k{}^-}, \quad (110)$$

$$I_{kk'}{}^{(3)}=\frac{2\epsilon^2}{\pi}\int_{-\infty}^{\infty}dE\sum_{k''}\frac{|t_{kk''}{}^+|^2|t_{k''k'}{}^+|^2}{|d_k{}^+|^2|d_{k'}{}^+|^2|d_{k''}{}^+|^2}. \quad (111)$$

Since $\langle L_{kk'}(E)\rangle$ is a smooth function of E, the technique described in connection with (102) enables us to evaluate it at once. We have

$$I_{kk'}{}^{(0)}=(2\pi\delta(\omega_{kk'})\langle L_{kk'}(\epsilon_k)\rangle)^{\frac{1}{2}}. \quad (112)$$

This gives rise to a term in $A_k{}^{(2)}$ which is just of the form of $A_k{}^{(1)}$ with N being replaced by $N^2/2$ (the number of pairs) and $2\pi\delta(\omega_{kk'})|t_{kk'}{}^+(\epsilon_k)|^2$ by $2\pi\delta(\omega_{kk'})\langle L_{kk'}(\epsilon_k)\rangle$. For this reason we shall refer to the contribution from (112) as the "true" two particle scattering contribution.

It is easy to see from the explicit expression for $\langle L_{kk'}\rangle$ that it is proportional to $1/\Omega^3$. It therefore gives a contribution to $\mathfrak{L}_k$ which is proportional to n^2. Similarly, it is seen at once that the other terms in (107) also give a contribution which is proportional to n^2.

The integrals (109) and (110) cannot be evaluated so simply because of the extra factor of $1/d_k{}^-$, which becomes very large at $E=\epsilon_k$. They are best evaluated by using the same contour integration techniques as were used in evaluating $J_{kk'}{}^{(1)}$. For $I_{kk'}{}^{(1)}$ this gives at once

$$I_{kk'}{}^{(1)}=-\frac{i}{x}\left[\frac{\alpha(\epsilon_k)}{x-is}+\frac{is\alpha(\epsilon_{k'})}{(x+is)^2}\right]+O(s), \quad (113)$$

where

$$\alpha(E)=t_{kk'}(E^+)t_{k'k}(E-is)t_{kk}(E-is). \quad (114)$$

Writing (113) as

$$I_{kk'}{}^{(1)}=-\frac{i}{x}\left[\frac{1}{x-is}+\frac{is}{(x+is)^2}\right]\alpha(\epsilon_k)\times\frac{s}{(x+is)^2}\left[\frac{\alpha(\epsilon_{k'})-\alpha(\epsilon_k)}{x}\right] \quad (115)$$

to the order in s we need, the last term of (115) vanishes. This may be seen as follows:

$$s\frac{1}{(x+is)^2}=\frac{s}{x^2+s^2}-\frac{2s^3}{(x^2+s^2)^2}-\frac{2is^2x}{(x^2+s^2)^2}. \quad (116)$$

However,

$$\lim_{s\to 0}\frac{s}{x^2+s^2}=\pi\delta(x), \quad (117)$$

$$\lim_{s\to 0}\frac{s^3}{(x^2+s^2)^2}=\frac{\pi}{2}\delta(x), \quad (118)$$

$$\lim_{s\to 0}\frac{2xs}{(x^2+s^2)^2}=-\pi\delta'(x), \quad (119)$$

and $[\alpha(\epsilon_{k'})-\alpha(\epsilon_k)]/x$ remains finite as $x\to 0$, so that

$$\lim_{s\to 0}\left[s\frac{1}{(x+is)^2}\right]\to\pi\delta(x)-\pi\delta(x)=0. \quad (120)$$

Therefore

$$I_{kk'}{}^{(1)}=-\frac{i}{x}\left(\frac{1}{x-is}+\frac{is}{(x+is)^2}\right)\alpha(\epsilon_k)=i\left(\frac{x^2+3s^2+2isx}{(x^2+s^2)^2}\right)\alpha(\epsilon_k)=\pi\alpha(\epsilon_k)\delta'(x)+i\alpha(\epsilon_k)\frac{x^2+3s^2}{(x^2+s^2)^2}, \quad (121)$$

using (119). From (117) and (118) we see that for small s the last term of (121) behaves like $1/s$.

Using now the same type of symmetrization as that of (95), and a little algebra, we obtain

$$I_{kk'}{}^{(1)}=\pi\left[\frac{\partial[\delta(E-\epsilon_{k'})|t_{kk'}{}^+(E)|^2t_{kk}{}^-(E)]}{\partial E}\right]_{E=\epsilon_k}+i\frac{x^2+3s^2}{(x^2+s^2)^2}|t_{kk'}{}^+(\epsilon_k)|^2t_{kk}{}^-(\epsilon_k), \quad (122)$$

give rise to a term proportional to ϵ. Since we only need $J_{kk'}{}^{(2)}$ to the zeroth power of ϵ, the bound states contribute nothing to our result. In the evaluation of the integrals we may therefore use the multiple scattering expansion, but treat t as if there were no bound states.

[7] The other terms correspond to the part of the scattering from two centers which does not drop off sufficiently rapidly with the distance between centers for the ensemble average to exist in the limit $\epsilon\to 0$.

and

$$I_{kk'}{}^{(2)}=\pi\left[\frac{\partial[\delta(E-\epsilon_k)|t_{kk'}{}^{+}(E)|^2 t_{k'k}{}^{-}(E)]}{\partial E}\right]_{E=\epsilon_{k'}} +i\frac{x^2+3s^2}{(x^2+s^2)^2}|t_{kk'}{}^{+}(\epsilon_{k'})|^2 t_{k'k}{}^{-}(\epsilon_{k'}). \quad (123)$$

Finally, we may treat $I_{kk'}{}^{(3)}$ in a similar fashion. The contour integration gives at once

$$I_{kk'}{}^{(3)}=s\sum_{k''}\left\{\frac{\beta(\epsilon_k)}{xz(x-is)(z+is)} +\frac{\beta(\epsilon_{k'})}{yx(y-is)(x+is)}+\frac{\beta(\epsilon_{k''})}{zy(z-is)(y+is)}\right\}, \quad (124)$$

where

$$x\equiv\epsilon_k-\epsilon_{k'},\quad y\equiv\epsilon_{k'}-\epsilon_{k''},\quad z\equiv\epsilon_{k''}-\epsilon_k,\quad x+y+z=0, \quad (125)$$

and

$$\beta(E)\equiv t_{kk''}(E^+)t_{k''k}(E-is)t_{k''k'}(E^+)t_{k'k''}(E-is). \quad (126)$$

Writing

$$I_{kk'}{}^{(3)}=s\sum_{k''}\left\{\beta(\epsilon_k)\left[\frac{1}{xz(x-is)(z+is)} +\frac{1}{yx(y-is)(x+is)}+\frac{1}{zy(z-is)(y+is)}\right] +\frac{[\beta(\epsilon_{k'})-\beta(\epsilon_k)]}{yx(y-is)(x+is)}+\frac{\beta(\epsilon_{k''})-\beta(\epsilon_k)}{zy(z-is)(y+is)}\right\}, \quad (127)$$

and making repeated use of the type of analysis which follows (115), we obtain

$$I_{kk'}{}^{(3)}=\sum_{k''}\left\{s\frac{x^2+y^2+z^2+6s^2}{(x^2+s^2)(y^2+s^2)(z^2+s^2)}\beta(\epsilon_k) +2\pi\delta(y)\frac{\beta(\epsilon_{k'})-\beta(\epsilon_k)}{(x+is)^2}\right\}. \quad (128)$$

When we use (117), (118), and (119), this becomes

$$I_{kk'}{}^{(3)}=\sum_{k''}\left\{s\frac{x^2+y^2+z^2+6s^2}{(x^2+s^2)(y^2+s^2)(z^2+s^2)}\beta(\epsilon_k) +2\pi i\delta(x)\delta(y)\left[\frac{\partial\beta(E)}{\partial E}\right]_{E=\epsilon_k} -2\pi\delta(y)P\left(\frac{1}{x}\right)\frac{\beta(\epsilon_k)-\beta(\epsilon_{k'})}{x}\right\}, \quad (129)$$

where $P(1/x)$ is the Cauchy principle value of $1/x$.

Using again the same sort of symmetrization as in (95), and noting that

$$s\frac{x^2+y^2+z^2+6s^2}{(x^2+s^2)(y^2+s^2)(z^2+s^2)}=\frac{4\pi^2}{s}\delta(y)\delta(x)+O(1), \quad (130)$$

we find at once

$$I_{kk'}{}^{(3)}=\sum_{k''}\left\{s\frac{x^2+y^2+z^2+6s^2}{(x^2+s^2)(y^2+s^2)(z^2+s^2)}|t_{kk''}{}^{+}(\epsilon_k)|^2|t_{k''k'}{}^{+}(\epsilon_k)|^2-2\pi\delta(y)P\left(\frac{1}{x}\right) \times\frac{|t_{kk''}{}^{+}(\epsilon_k)|^2|t_{k''k'}{}^{+}(\epsilon_k)|^2-|t_{kk''}{}^{+}(\epsilon_{k'})|^2|t_{k''k'}{}^{+}(\epsilon_{k'})|^2}{x}\right\}. \quad (131)$$

We now must put all these expressions together to compute $A_k{}^{(2)}$. From (64) and (65)

$$A_k{}^{(2)}=\sum_{k'}K_{kk'}(f_{k'}-f_k), \quad (132)$$

where

$$K_{kk'}=J_{kk'}{}^{(2)}+\frac{1}{is}\sum_{k''}\{J_{kk'}{}^{(1)}J_{kk''}{}^{(1)} +J_{kk'}{}^{(1)}J_{k'k''}{}^{(1)}-J_{kk''}{}^{(1)}J_{k''k'}{}^{(1)}\}. \quad (133)$$

From (100) and (107) this may be written as

$$K_{kk'}=iN^2\left\{I_{kk'}{}^{(0)}+I_{kk'}{}^{(1)}+I_{kk'}{}^{(1)*} +I_{kk'}{}^{(2)}+I_{kk'}{}^{(2)*}+I_{kk'}{}^{(3)} +\frac{1}{s}\sum_{k''}(\sigma_{kk'}\sigma_{kk''}+\sigma_{kk'}\sigma_{k'k''}-\sigma_{kk''}\sigma_{k''k'})\right\}. \quad (134)$$

We next have to show that the apparent $1/s$ singularity in $K_{kk'}$ cancels out, and then calculate the limit of the remainder as $s\to 0$. We shall first rewrite $I_{kk'}{}^{(1)}+I_{kk'}{}^{(1)*}$. Put

$$t_{kk}{}^{-}(E)=\Delta_k(E)+ir_k(E),$$
$$t_{kk}{}^{+}(E)=\Delta_k(E)-ir_k(E).$$

Then

$$I_{kk'}{}^{(1)}+I_{kk'}{}^{(1)*}=2\pi\left[\frac{\partial(\delta(E-\epsilon_{k'})\Delta_k(E)|t_{kk'}{}^{+}(E)|^2)}{\partial E}\right]_{E=\epsilon_k} -2\frac{x^2+3s^2}{(x^2+s^2)^2}|t_{kk'}{}^{+}(\epsilon_k)|^2 r_k(\epsilon_k). \quad (135)$$

Noticing that

$$\frac{x^2+3s^2}{(x^2+s^2)^2}=\frac{2}{x^2+s^2}-\frac{x^2-s^2}{(x^2+s^2)^2}=\frac{2}{x^2+s^2}+P'\left(\frac{1}{x}\right), \quad (136)$$

where

$$P'\left(\frac{1}{x}\right)=\lim_{s\to 0}\left[-\frac{x^2-s_z}{(x^2+s^2)^2}\right]$$
$$=\lim_{s\to 0}\frac{\partial}{\partial x}\left[\text{Real part}\frac{1}{(x+is)}\right], \quad (137)$$

we may write

$$\frac{x^2+3s^2}{(x^2+s^2)^2}|t_{kk'}{}^+(\epsilon_k)|^2$$
$$=\frac{2}{(x^2+s^2)}|t_{kk'}{}^+(\epsilon_k)|^2+P'\left(\frac{1}{x}\right)|t_{kk'}{}^+(\epsilon_k)|^2$$
$$=\frac{1}{x^2+s^2}[|t_{kk'}{}^+(\epsilon_k)|^2+|t_{kk'}{}^+(\epsilon_{k'})|^2]$$
$$+\frac{1}{x^2+s^2}[|t_{kk'}{}^+(\epsilon_k)|^2-|t_{kk'}{}^+(\epsilon_{k'})]$$
$$+P'\left(\frac{1}{x}\right)|t_{kk'}{}^+(\epsilon_k)|^2$$
$$=\frac{\sigma_{kk'}}{s}-\sum_b|(k|b)|^2|(k'|b)|^2$$
$$+P\left(\frac{1}{x}\right)\frac{|t_{kk'}{}^+(\epsilon_k)|^2-|t_{kk'}{}^+(\epsilon_{k'})|^2}{x}$$
$$+P'\left(\frac{1}{x}\right)|t_{kk'}{}^+(\epsilon_k)|^2. \quad (138)$$

In deriving (138) we have made use of (100). From the optical theorem (C33), we have

$$2r_k(\epsilon_k)=\sum_{k''}\sigma_{kk''}+s\left[\frac{\partial\Delta_k(E)}{\partial E}\right]_{E=\epsilon_k}, \quad (C33)$$

so that we may write

$$2\frac{x^2+3s^2}{(x^2+s^2)^2}|t_{kk'}{}^+(\epsilon_k)|^2r_k(\epsilon_k)$$
$$=-\frac{1}{s}\sum_{k''}\sigma_{kk'}\sigma_{kk''}+2\pi\delta(x)|t_{kk'}{}^+(\epsilon_k)|^2$$
$$\times\left[\frac{\partial\Delta_k(E)}{\partial E}\right]_{E=\epsilon_k}+2r_k(\epsilon_k)\left[P'\left(\frac{1}{x}\right)|t_{kk'}{}^+(\epsilon_k)|^2\right.$$
$$+P\left(\frac{1}{x}\right)\frac{|t_{kk'}{}^+(\epsilon_k)|^2-|t_{kk'}{}^+(\epsilon_{k'})|^2}{x}$$
$$\left.-\sum_b|(k|b)|^2|(k'|b)|^2\right]. \quad (139)$$

Substituting (139) in (135), we have

$$I_{kk'}{}^{(1)}+I_{kk'}{}^{(1)*}=-\frac{1}{s}\sum_{k''}\sigma_{kk'}\sigma_{kk''}+2\pi\Delta_k(\epsilon_k)$$
$$\times\left[\frac{\partial[\delta(E-\epsilon_{k'})|t_{kk'}{}^+(E)|^2]}{\partial E}\right]_{E=\epsilon k}$$
$$-2r_k(\epsilon_k)\left[P'\left(\frac{1}{x}\right)|t_{kk'}{}^+(\epsilon_k)|^2+P\left(\frac{1}{x}\right)\right.$$
$$\times\frac{|t_{kk'}{}^+(\epsilon_k)|^2-|t_{kk'}{}^+(\epsilon_{k'})|^2}{x}$$
$$\left.-\sum_b|(k|b)|^2|(k'|b)|^2\right]. \quad (140)$$

Similarly

$$I_{kk'}{}^{(2)}+I_{kk'}{}^{(2)}=-\frac{1}{s}\sum_{k''}\sigma_{kk'}\sigma_{k'k''}+2\pi\Delta_{k'}(\epsilon_{k'})$$
$$\times\left[\frac{\partial[\delta(E-\epsilon_k)|t_{kk'}{}^+(E)|^2]}{\partial E}\right]_{E=\epsilon_{k'}}$$
$$-2r_{k'}(\epsilon_{k'})\left[P'\left(\frac{1}{x}\right)|t_{kk'}{}^+(\epsilon_{k'})|^2-P\left(\frac{1}{x}\right)\right.$$
$$\times\frac{|t_{kk'}{}^+(\epsilon_k)|^2-|t_{kk'}{}^+(\epsilon_{k'})|^2}{x}$$
$$\left.-\sum_b|(k|b)|^2|(k'|b)|^2\right]. \quad (141)$$

If all these results are substituted in (134) we find indeed that the $1/s$ terms drop out and—after very considerable algebra—we are left with the following result:

$$K_{kk'}=iN^2\{I_{kk'}{}^{(0)}+\alpha_{kk'}{}^{(1)}+\alpha_{kk'}{}^{(2)}+\alpha_{kk'}{}^{(3)}\}, \quad (142)$$

where

$$\alpha_{kk'}{}^{(1)}\equiv i\sum_{k''}\left\{\frac{1}{(x-is)(y+is)(z+is)}\right.$$
$$\left.-\frac{1}{(x+is)(y-is)(z-is)}\right\}$$
$$\times|t_{kk''}{}^+(\epsilon_k)|^2|t_{k''k'}{}^+(\epsilon_{k'})|^2, \quad (143)$$

$$\mathfrak{A}_{kk'}^{(2)}=2\Big\{|t_{kk'}^{+}(\epsilon_{k'})|^2\times\Big[\pi\Delta_k(\epsilon_k)\delta'(x)-r_k(\epsilon_k)P'\Big(\frac{1}{x}\Big)\Big]+|t_{kk'}^{+}(\epsilon_k)|^2\times\Big[-\pi\Delta_{k'}(\epsilon_{k'})\delta'(x)-r_{k'}(\epsilon_{k'})P'\Big(\frac{1}{x}\Big)\Big]\Big\}, \quad (144)$$

$$=\frac{1}{i}\Big\{|t_{kk'}^{+}(\epsilon_{k'})|^2\Big[-\frac{\Delta_k(\epsilon_k)-ir_k(\epsilon_k)}{(\epsilon_k-\epsilon_{k'}-is)^2}\Big]+|t_{kk'}^{+}(\epsilon_k)|^2\times\Big[-\frac{\Delta_{k'}(\epsilon_{k'})-ir_{k'}(\epsilon_{k'})}{(\epsilon_{k'}-\epsilon_k-is)^2}\Big]-\text{c.c.}\Big\}, \quad (145)$$

$$\mathfrak{A}_{kk'}^{(3)}=-\sum_{k''}\{w_{kk''}[|(k''|b)|^2-|(k|b)|^2]|(k'|b)|^2+w_{k''k'}[|(k''|b)|^2-|(k'|b)|^2]|(k|b)|^2\}. \quad (146)$$

The first three terms in (142) also appeared in I, where they were computed to the fourth order in λ. The last term, which refers to bound states, did not appear at all in the perturbation theoretic calculations of I.

Again, as in I, $\mathfrak{A}_{kk'}^{(2)}$ may be roughly interpreted via (145) as being due to a shift in the unperturbed energy of a state k by an amount $N\Delta_k(\epsilon_k)$ and a natural lifetime for this state of $\sum_{k''} w_{kk''}$.

IV. CALCULATION OF THE FIELD TERMS

The field terms $eE_\alpha^0 M_{\alpha k}$ of (84) may be written

$$eE_\alpha^0 M_{\alpha k}=C_k-(B_k^{(1)}+B_k^{(2)}+\cdots) \quad (147)$$

from (29) and (83). We only want (147) to the first order in n, so that all we need is

$$eE_\alpha^0 M_{\alpha k}^{(0)}=C_k^{(0)}, \quad (148)$$

$$eE_\alpha^0 M_{\alpha k}^{(1)}=C_k^{(1)}-B_k^{(1)}. \quad (149)$$

The commutator C is investigated in detail in Appendix B. From (B30) we have

$$C_k^{(0)}=ieE_\alpha^0\partial\rho^0(\epsilon_k)/\partial k_\alpha, \quad \text{(B30)}$$

so that

$$M_{\alpha k}^{(0)}=i\partial\rho^0(\epsilon_k)/\partial k_\alpha. \quad (150)$$

The expression for $C_k^{(1)}$ is given by (B31). Before we make use of this, however, it is necessary to evaluate $B_k^{(1)}$. By means of (81), (82), (B35), and (C4), we have at once

$$B_k^{(1)}=-NieE_\alpha^0\frac{\epsilon}{\pi}\int_{-\infty}^{\infty}\frac{dE}{|d_k^{+}|^2}\Big\{\sum_{k'}\Big[\frac{t_{kk'}^{+}P_{k'k}^{\alpha}}{d_{k'}^{+}}+\frac{P_{kk'}^{\alpha}t_{k'k}^{-}}{d_{k'}^{-}}\Big]+\sum_{k',k''}\frac{t_{kk'}^{+}P_{k'k''}^{\alpha}t_{k''k}^{-}}{d_{k'}^{+}d_{k''}^{-}}\Big\}, \quad (151)$$

where

$$P_{kk'}^{\alpha}=\sum_b\rho^0(\epsilon_b)\Big[\frac{\partial(k|b)}{\partial k_\alpha}(b|k')+(k|b)\frac{\partial(b|k')}{\partial k_\alpha'}\Big]+\Big[\frac{\partial}{\partial k_\alpha}+\frac{\partial}{\partial k_\alpha'}\Big]\tilde{D}_{kk'}, \quad (152)$$

$$\tilde{D}_{kk'}=\frac{1}{2\pi i}\int_0^{\infty}dE\rho^0(E)\Big[\frac{t_{kk'}^{-}(E)}{d_k^{-}d_{k'}^{-}}-\frac{t_{kk'}^{+}(E)}{d_k^{+}d_{k'}^{+}}\Big]. \quad (153)$$

The integral in (151) may be evaluated by contour integration as in all previous cases. After some simplifications this yields

$$B_k^{(1)}=-NieE_\alpha^0\Big\{\sum_{k'}\Big[\frac{t_{kk'}^{+}(\epsilon_k)P_{k'k}^{\alpha}}{x+is}+\frac{P_{kk'}^{\alpha}t_{k'k}^{-}(\epsilon_k)}{x-is}\Big]-\sum_{k',k''}\frac{t_{kk'}^{+}(\epsilon_k)P_{k'k''}^{\alpha}t_{k''k}^{-}(\epsilon_k)}{(x+is)(z+is)}+\sum_b|(k|b)|^2\sum_{k',k''}(b|k')P_{k'k''}^{\alpha}(k''|b)\Big\}. \quad (154)$$

Therefore, by (B31), we have

$$M_{\alpha k}^{(1)}=iN\Big\{\delta\frac{\partial\rho^0(\epsilon_k)}{\partial\alpha}+\sum_b\rho^0(\epsilon_b)\frac{\partial|(k|b)|^2}{\partial k_\alpha}+\frac{\partial\tilde{D}_{kk}}{\partial k_\alpha}+\sum_{k'}\Big[\frac{t_{kk'}^{+}(\epsilon_k)P_{k'k}^{\alpha}}{x+is}+\frac{P_{kk'}^{\alpha}t_{k'k}^{-}(\epsilon_k)}{x-is}\Big]-\sum_{k',k''}\frac{t_{kk'}^{+}(\epsilon_k)P_{k'k''}^{\alpha}t_{k''k}^{-}(\epsilon_k)}{(x+is)(z+is)}+\sum_b|(k|b)|^2\sum_{k',k''}(b|k')P_{k'k''}^{\alpha}(k''|b)\Big\}. \quad (155)$$

Putting (152) in (155) we find—after some work—that the $\rho^0(\epsilon_b)$ terms cancel out completely. This is to be expected since if only the single-center bound states were occupied there could be no conductivity. We then have

$$M_{\alpha k}^{(1)}=iN\Big\{\delta\frac{\partial\rho^0(\epsilon_k)}{\partial k_\alpha}+\frac{\partial\tilde{D}_{kk}}{\partial k_\alpha}-\sum_b\sum_{k'}|(k|b)|^2|(b|k')|^2\frac{\partial\rho^0(\epsilon_{k'})}{\partial k_\alpha'}+\sum_{k'}\Big[\frac{t_{kk'}^{+}(\epsilon_k)\tilde{P}_{k'k}^{\alpha}}{x+is}+\frac{\tilde{P}_{kk'}^{\alpha}t_{k'k}^{-}(\epsilon_k)}{x-is}\Big]-\sum_{k',k''}\frac{t_{kk'}^{+}(\epsilon_k)\tilde{P}_{k'k''}^{\alpha}t_{k''k}^{-}(\epsilon_k)}{(x+is)(z+is)}\Big\}, \quad (156)$$

where

$$\tilde{P}_{kk'}{}^{\alpha}=\left[\frac{\partial}{\partial k_\alpha}+\frac{\partial}{\partial k_\alpha}\right]\tilde{D}_{kk'}.$$

This expression is easily seen to be proportional to the density n.

It does not seem possible to go appreciably further with (156), without a more detailed knowledge of the single-center scattering operator t.

V. THE TRANSPORT EQUATION

We now collect the results of the previous sections in order to obtain the transport equation in the lowest order in the density, and the first correction to it. From (85) and (87) the lowest order equation is

$$\frac{1}{n}A_k{}^{(1)}=eE_\alpha{}^0M_{\alpha k}{}^{(0)}. \tag{157}$$

Making use of (103) and (150), (157) becomes

$$\sum_{k'}\Omega w_{kk'}(f_{k'}{}^{(0)}-f_k{}^{(0)})=eE_\alpha{}^0\frac{\partial\rho^0(\epsilon_k)}{\partial k_\alpha}. \tag{158}$$

This is just the usual Boltzmann equation in our notation, and we have therefore proved that in the limit of low density it is valid.

The next order is given by (86). Making use of (132), this becomes

$$i\sum_{k'}\Omega w_{kk'}(f_{k'}{}^{(1)}-f_k{}^{(1)})+\frac{1}{n}\sum_{k'}K_{kk'}(f_{k'}{}^{(0)}-f_k{}^{(0)})=eE_\alpha{}^0M_{\alpha k}{}^{(1)}. \tag{159}$$

If we think of $f_k{}^{(0)}$ as given [obtained by solving (158)] then the second term on the left-hand side of (159) may be regarded as an inhomogeneity. Therefore (159) as an equation for $f_k{}^{(1)}$ is exactly of the same form as (158) for $f_k{}^{(0)}$, with a somewhat different inhomogeneity.

In general these equations are *integral equations*, and nothing can be done until more is known about the kernel $w_{kk'}$. If, however, the scattering centers have spherically symmetric potentials, then, as is well known for (158), the equations may be solved at once. This is because in this case $w_{kk'}$ is invariant under simultaneous rotations of k and k' and $M_{\alpha k}$, being a vector, must be of the form $k_\alpha\mu(|k|)$. Therefore $f_k{}^{(0)}$ must have the form

$$f_k{}^{(0)}=eE_\alpha{}^0k_\alpha a^{(0)}(|k|). \tag{160}$$

The fact that $w_{kk'}$ contains a $\delta(\omega_{kk'})$ then enables one to take $a(|k|)$ outside the summation and solve for it at once, giving

$$a^{(0)}(|k|)=\frac{2}{\Omega}\frac{-\partial\rho^0(\epsilon_k)}{\epsilon_k\,\partial\epsilon_k}\frac{1}{\sum_{k'}w_{kk'}[(\mathbf{k}\cdot\mathbf{k}')-k^2]}. \tag{161}$$

The identical process may be carried out for $f_k{}^{(1)}$ since it involves the same kernel $w_{kk'}$. Therefore for the case of spherically symmetric scattering centers the solution of the transport equation can be obtained explicitly.

Writing

$$f_k{}^{(1)}=eE_\alpha{}^0k_\alpha a^{(1)}(|k|), \tag{162}$$

we obtain at once

$$a^{(1)}(|k|)=\frac{k_\alpha M_{\alpha k}{}^{(1)}-\frac{1}{n_{k'}}[(\mathbf{k}\cdot\mathbf{k}')a^{(0)}(|k'|)-k^2a^{(0)}(|k|)]}{i\Omega\sum_{k'}w_{kk'}(\mathbf{k}\cdot\mathbf{k}'-k^2)}. \tag{163}$$

Here $M_{\alpha k}{}^{(1)}$ and $K_{kk'}$ are defined in (156) and (142), respectively.

The order of magnitude of the n^2 correction, for a simple case, has been mentioned at the end of Sec. III of I.

APPENDIX A. EXPANSION OF SCATTERING OPERATOR

The scattering operator T satisfies the operator equation

$$T=H'\left(1+\frac{1}{d}T\right)=(\sum_l\varphi_l)+(\sum_l\varphi_l)\frac{1}{d}T. \tag{A1}$$

Now define a sequence of operators T_l, T_{lm}, $\cdots$ which satisfy

$$T_l=\varphi_l\left(1+\frac{1}{d}T_l\right), \tag{A2}$$

$$T_{lm}=(\varphi_l+\varphi_m)\left(1+\frac{1}{d}T_{lm}\right), \tag{A3}$$

$$T_{lmn}=(\varphi_l+\varphi_m+\varphi_n)\left(1+\frac{1}{d}T_{lmn}\right), \text{ etc.,} \tag{A4}$$

where $l\neq m\neq n$, etc. T_l is the scattering operator if only one scatterer were present and located at r_l, T_{lm} is the scattering operator if scatterers were present only at r_l and r_m, etc.

Now we shall try to solve (A1) in terms of the operators defined by (A2), (A3), and (A4). To do this let us write for T the following expression:

$$T=\sum_l Q_l+\frac{1}{2!}\sum_{lm}{}'Q_{lm}+\frac{1}{3!}\sum_{lmn}{}'Q_{lmn}+\cdots, \tag{A5}$$

where Q_l depends only on the position of the lth scatterer, Q_{lm} on the l and m scatterers, etc. The prime on the summation means that *none* of the indices are to be taken equal (in the second term $l=m$, in the third $l=m=n$, etc). Further, Q_{lmn} is assumed completely symmetric in all the indices since any nonsymmetric

part would vanish under the summation. If we substitute (A5) into (A1), we get equations for the Q's. That is,

$$\sum_l Q_l+\frac{1}{2!}\sum_{lm}{}' Q_{lm}+\frac{1}{3!}\sum_{lmn}{}' Q_{lmn}+\cdots$$

$$=\sum_l \varphi_l+(\sum_p \varphi_p)\frac{1}{d}\left(\sum_l Q_l+\frac{1}{2!}\sum_{lm}{}' Q_{lm}+\cdots\right). \quad \text{(A6)}$$

Equating terms in (A6) which refer to *one* center, then those which refer to two distinct centers, etc., we obtain

$$\sum_l\left(Q_l-\varphi_l-\varphi_l\frac{1}{d}Q_l\right)=0, \quad \text{(A7)}$$

$$\sum_{lm}{}'\left[\frac{1}{2!}Q_{lm}-\varphi_m\frac{1}{d}Q_l-\frac{1}{2!}\left(\varphi_l\frac{1}{d}Q_{lm}+\varphi_m\frac{1}{d}Q_{lm}\right)\right]=0, \quad \text{(A8)}$$

etc.

Comparing (A7) and (A2), we see that (A7) is identically satisfied if we choose

$$Q_l=T_l. \quad \text{(A9)}$$

In (A8), if we symmetrize the second term we see that (A8) is satisfied when

$$Q_{lm}=\varphi_m\frac{1}{d}Q_l+\varphi_l\frac{1}{d}Q_m+(\varphi_l+\varphi_m)\frac{1}{d}Q_{lm}. \quad \text{(A10)}$$

Comparing (A10) with (A3) and (A2), we see at once that

$$Q_{lm}=T_{lm}-(Q_l+Q_m)=T_{lm}-T_l-T_m. \quad \text{(A11)}$$

Similarly

$$\begin{aligned}Q_{lmn}&=T_{lmn}-(Q_{lm}+Q_{mn}+Q_{nl}+Q_l+Q_m+Q_n)\\&=T_{lmn}-T_{lm}-T_{mn}-T_{nl}+T_l+T_m+T_n.\end{aligned} \quad \text{(A12)}$$

It is very easy to continue this process and establish expressions analogous to (A12) for arbitrarily many centers, but for our purposes the two terms (9) and (11) will suffice.

APPENDIX B. EXPANSION OF THE COMMUTATOR

We obtain in this appendix an expression for the quantity

$$C=-cE_\alpha{}^0[\rho,x_\alpha] \quad \text{(B1)}$$

analogous to the "virial" expansion used for the other quantities of interest. From Eq. (9) we see that we must expand $e^{-\beta H}$. This is done most conveniently through the identity

$$e^{-\beta H}=\frac{1}{2\pi i}\int_\gamma dz\frac{e^{-\beta z}}{z-H}=\frac{1}{2\pi i}\int_\gamma dzR(z)e^{-\beta z}, \quad \text{(B2)}$$

where γ is the contour shown in Fig. 2, and ϵ_0 is the smallest eigenvalue of H.

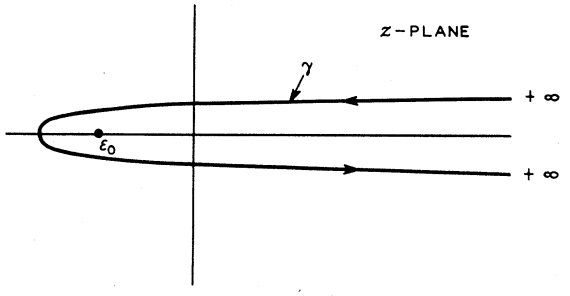

FIG. 2. Contour γ for Eq. (B2).

Upon using (49), (B2) becomes

$$\begin{aligned}e^{-\beta H}&=\frac{1}{2\pi i}\int_\gamma dz\left\{\frac{1}{d(z)}+\frac{1}{d(z)}T(z)\frac{1}{d(z)}\right\}e^{-\beta z}\\&=e^{-\beta H_0}+\frac{1}{2\pi i}\int_\gamma dz\frac{1}{d(z)}T(z)\frac{1}{d(z)}e^{-\beta z},\end{aligned} \quad \text{(B3)}$$

on evaluating the contour integral for the first term.

Making use of (66), we now have

$$\rho=\rho_0=\sum_l \rho_l+\frac{1}{2!}\sum_{lm}{}' \rho_{lm}+\cdots, \quad \text{(B4)}$$

where

$$\rho_0=Ke^{-\beta H_0}, \quad \text{(B5)}$$

$$\rho_l=\frac{K}{2\pi i}\int_\gamma dz\frac{1}{d}T_l\frac{1}{d}e^{-\beta z},$$

$$\rho_{lm}=\frac{K}{2\pi i}\int_\gamma dz\frac{1}{d}(T_{lm}-T_l-T_m)\frac{1}{d}e^{-\beta z}, \quad \text{(B6)}$$

etc. The expansion (B4) is not quite a density expansion since the quantity K itself as determined by (10) should also be expanded in powers of the density. Substituting (B4) in (B1) we obtain

$$C=C_0+\sum_l C_l+\frac{1}{2!}\sum_{lm}{}' C_{lm}+\cdots, \quad \text{(B7)}$$

where

$$C_0=eE_\alpha{}^0[\rho_0,x_\alpha], \quad \text{(B8)}$$

$$C_l=eE_\alpha{}^0[\rho_l,x_\alpha], \quad \text{(B9)}$$

etc. Therefore C has also been developed in a virial-like expansion.

In the k representation, C is given by

$$C_{kk'}=ieE_\alpha{}^0\left(\frac{\partial}{\partial k_\alpha}+\frac{\partial}{\partial k_\alpha{}'}\right)\rho_{kk'}, \quad \text{(B10)}$$

[see I, Eq. (A19)].

Important for the discussion of $\Gamma_k{}^{(2)}$ is the fact that since ρ_0 is diagonal in the k-representation so is C_0, and

therefore

$$C'=\sum_l C_l'+\frac{1}{2!}\sum_{lm}' C_{lm}'+\cdots. \tag{B11}$$

The diagonal elements of C are given by

$$C_k=ieE_\alpha^0\frac{\partial\rho_{kk}}{\partial k_\alpha}, \tag{B12}$$

[see I, Eq. (A22)].

We shall push the evaluation of these formulas one step beyond the lowest order, since this is all we need for the purposes of this paper. Let us write to this order

$$K=K_0(1+N\delta), \tag{B13}$$

where K_0 is determined by

$$K_0^{-1}=\mathrm{tr}(e^{-\beta H_0})=\sum_k e^{-\beta\epsilon_k}. \tag{B14}$$

Further, let us define

$$\rho^0(H_0)=K_0e^{-\beta H_0}. \tag{B15}$$

Then

$$\rho_0=(1+N\delta)\rho^0,$$

and

$$\rho_{0kk'}=(1+N\delta)\rho^0(\epsilon_k)\delta_{kk'}. \tag{B16}$$

Therefore, to the order in question,

$$\rho_{kk'}=(1+N\delta)\rho^0(\epsilon_k)\delta_{kk'}+\frac{1}{2\pi i}\int_\gamma dz\frac{\sum_l(T_l)_{kk'}}{d_kd_{k'}}\rho^0(z). \tag{B17}$$

The constant δ is determined by

$$\sum\rho_{kk}=1. \tag{B18}$$

Now we have (see Appendix C for properties of the scattering matrix)

$$(T_l)_{kk'}=e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_l}t_{kk'}, \tag{B19}$$

where t is the scattering operator for a single center located at the origin. Therefore (B17) may be written

$$\rho_{kk'}=(1+N\delta)\rho^0(\epsilon_k)\delta_{kk'}+S_{kk'}D_{kk'}, \tag{B20}$$

with

$$S_{kk'}\equiv\sum_l e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_l}, \tag{B21}$$

$$D_{kk'}\equiv\frac{1}{2\pi i}\int_\gamma dz\frac{t_{kk'}}{d_kd_{k'}}\rho^0(z). \tag{B22}$$

The quantity δ is given by (B18) as

$$\delta=-\sum_k D_{kk}. \tag{B23}$$

Since $t_{kk'}$ is proportional to $1/\Omega$, $D_{kk'}$ is proportional to $1/\Omega^2$ and therefore δ is proportional to $1/\Omega$, giving a correction proportional to the density of impurities, as anticipated.

From Appendix C we know that $t_{kk'}(z)$ is a regular function of z except for isolated simple poles on the negative real axis (corresponding to possible bound states), and a branch cut along the positive real axis. Call t^+ the value of t at a distance ϵ above the positive real axis, and t^- its value at ϵ below. Further let the residue of t at a bound state $\epsilon_b(<0)$ be $r^{(b)}$. Then, deforming γ so that it encircles the poles at ϵ_b and is within ϵ ($\epsilon\to0$ eventually) of the real axis above and below, we obtain

$$D_{kk'}=\sum_b\rho^0(\epsilon_n)\frac{r_{kk'}^{(b)}}{(\epsilon_b-\epsilon_k)(\epsilon_b-\epsilon_{k'})}+\frac{1}{2\pi i}\times\int_0^\infty dE\rho^0(E)\left(\frac{t_{kk'}^-(E)}{d_k^-d_{k'}^-}-\frac{t_{kk'}^+(E)}{d_k^+d_{k'}^+}\right). \tag{B24}$$

The first term can be simplified by noting that

$$r_{kk'}^{(b)}=(\epsilon_b-\epsilon_k)(\epsilon_b-\epsilon_{k'})(k|b)(b|k'), \tag{B25}$$

where

$$(k|b)=\int\psi_k^*\psi_b dr=(b|k)^*, \tag{B26}$$

ψ_b being the normalized bound state wave function. Therefore

$$D_{kk'}=\sum_b\rho^0(\epsilon_b)(k|b)(b|k')+\frac{1}{2\pi i}\int_0^\infty dE\rho^0(E)\left[\frac{t_{kk'}^-(E)}{d_k^-d_{k'}^-}-\frac{t_{kk'}^+(E)}{d_k^+d_{k'}^+}\right]\equiv\sum_b\rho^0(\epsilon_b)(k|b)(b|k')+\tilde{D}_{kk'}. \tag{B27}$$

Not much more can be done with the integral $\tilde{D}_{kk'}$ without further knowledge of the scattering operator t.

For the diagonal elements of $\rho_{kk'}$, we have

$$\rho_{kk}=(1+N\delta)\rho^0(\epsilon_k)+ND_{kk}=\rho^0(\epsilon_k)+N\delta\rho^0(\epsilon_k)+ND_{kk}. \tag{B28}$$

The second and third terms are proportional to n, the first is independent of n. Therefore

$$C_k=ieE_\alpha^0\partial\rho_{kk}/\partial k_\alpha=C_k^{(0)}+C_k^{(1)}, \tag{B29}$$

$$C_k^{(0)}=ieE_\alpha^0\partial\rho^0(\epsilon_k)/\partial k_\alpha, \tag{B30}$$

$$C_k^{(1)}=NieE_\alpha^0\delta\left[\frac{\partial\rho^0(\epsilon_k)}{\partial k_\alpha}+\sum_b\rho^0(\epsilon_b)\frac{\partial|(k|b)|^2}{\partial k_\alpha}+\frac{\partial\tilde{D}_{kk}}{\partial k_\alpha}\right]. \tag{B31}$$

The off-diagonal elements are given by

$$\rho_{kk'}=S_{kk'}D_{kk'},\quad(k\neq k') \tag{B32}$$

so that

$$C_{kk'}=ieE_\alpha^0S_{kk'}\left(\frac{\partial}{\partial k_\alpha}+\frac{\partial}{\partial k_\alpha'}\right)D_{kk'},\quad(k\neq k') \tag{B33}$$

since $S_{kk'}$ is a function of $k-k'$ alone. Using (B27), we have finally

$$C_{kk'}\equiv ieE_\alpha{}^0\sum_l e^{-i(k-k')r_l}P_{kk'}{}^\alpha, \tag{B34}$$

where

$$P_{kk'}{}^\alpha=\sum_b \rho^0(\epsilon_b)\left[\frac{\partial(k|b)}{\partial k_\alpha}(b|k')+(k|b)\frac{\partial(b|k')}{\partial k_\alpha}\right]+\left(\frac{\partial}{\partial k_\alpha}+\frac{\partial}{\partial k_\alpha'}\right)\tilde{D}_{kk'}. \tag{B35}$$

APPENDIX C. PROPERTIES OF THE SCATTERING OPERATORS

We begin by discussing the scattering operator T_l for a single scatterer located at r_l. From Appendix A, Eq. (A2) we have

$$T_l=\varphi_l\left(1+\frac{1}{d}T_l\right). \tag{C1}$$

Taking matrix elements, and remembering that

$$(\varphi_l)_{kk'}+e^{-i(k-k')r_l}\varphi_{kk'} \tag{C2}$$

(where $\varphi_{kk'}$ is the matrix element of the potential for a scatterer at the origin), we have

$$(T_l)_{kk'}=e^{-i(k-k')r_l}\varphi_{kk'}+\sum_{k''}\varphi_{kk''}\frac{1}{d_{k''}}e^{-i(\mathbf{k}-\mathbf{k}'')\cdot\mathbf{r}_l}(T_l)_{k''k'}. \tag{C3}$$

This is satisfied by the ansatz

$$(T_l)_{kk'}=e^{-i(k-k')r_l}t_{kk'}, \tag{C4}$$

where t is independent of r_l. Substituting (C4) in (C3), we obtain

$$t=\varphi\left(1+\frac{1}{d}t\right), \tag{C5}$$

so that t is just the scattering operator for a scatterer located at the origin.

Similarly, starting with the scattering operator T_{lm} for scatterers at r_l and r_m, we can easily show (by just writing out the Eq. (A3) for T_{lm}) that

$$(T_{lm})_{kk'}=T_{kk'}(r)e^{-i(k-k')r_l}, \tag{C6}$$

where $r=r_m-r_l$, the distance between the two scatterers. $T_{kk'}(r)$ is just the scattering operator for a particle being scattered by two centers; one at the origin and one at r.

The quantity T_{lm} may be expressed in terms of T_l and T_m as follows.[8] Define operators M_l and M_m as the solutions of the coupled equations

$$M_l=1+\frac{1}{d}T_mM_m, \tag{C7}$$

$$M_m=1+\frac{1}{d}T_lM_l. \tag{C8}$$

Then

$$T_{lm}=T_lM_l+T_mM_m. \tag{C9}$$

Equation (C9) is verified by simply substituting (C9) in (A3) and making use of (C7), (C8) and (C1).

These relationships may be used to obtain the so-called *multiple-scattering* expression for T_{lm}. Assuming that T_l and T_m are in some sense small, we can solve (C7) and (C8) by iteration, obtaining

$$M_l=1+\frac{1}{d}T_m+\frac{1}{d}T_m\frac{1}{d}T_l+\frac{1}{d}T_m\frac{1}{d}T_l\frac{1}{d}T_m+\cdots, \tag{C10}$$

$$M_m=1+\frac{1}{d}T_l+\frac{1}{d}T_l\frac{1}{d}T_m+\frac{1}{d}T_l\frac{1}{d}T_m\frac{1}{d}T_l+\cdots. \tag{C11}$$

Substituting in (C9) gives

$$T_{lm}=T_l+T_m+T_l\frac{1}{d}T_m+T_m\frac{1}{d}T_l+T_l\frac{1}{d}T_m\frac{1}{d}T_l+T_m\frac{1}{d}T_l\frac{1}{d}T_m+\cdots. \tag{C12}$$

We shall also need some analytical properties of the scattering operators. Making use of (49) for the case of a single scattering center, we have

$$t=d\frac{1}{z-h}d-d, \tag{C13}$$

where

$$h=H_0+\varphi, \tag{C14}$$

the Hamiltonian of a particle in the presence of a single scatterer at the origin. Call the eigenfunctions and eigenvalues of h, ψ_ν, ϵ_ν respectively; i.e.,

$$h\psi_\nu=\epsilon_\nu\psi_\nu=(H_0+\varphi)\psi_\nu. \tag{C15}$$

In this representation (C13) becomes

$$t_{\nu\nu'}=\sum_{\nu''}\frac{d_{\nu\nu''}d_{\nu''\nu'}}{z-\epsilon_{\nu''}}-d_{\nu\nu'}. \tag{C16}$$

Transforming this back to the k-representation, we obtain

$$t_{kk'}=\sum_{\nu''}\frac{d_{k\nu''}d_{\nu''k'}}{z-\epsilon_{\nu''}}-d_k\delta_{kk''}, \tag{C17}$$

[8] See, for example, K. M. Watson, Phys. Rev. **89**, 575 (1952).

where

$$d_{k\nu''}=\int\psi_k^*d\psi_{\nu''}dr,\quad d_{\nu''k'}=\int\psi_{\nu''}^*d\psi_{k'}dr. \tag{C18}$$

Since ψ_k is an eigenfunction of d, we may write

$$\begin{aligned}d_{k\nu''}&=(k|\nu'')d_k,\\ d_{\nu''k'}&=(\nu''|k')d_{k'},\end{aligned} \tag{C19}$$

where $(k|\nu'')$ are the usual transformation coefficients

$$(k|\nu'')=\int\psi_k^*\psi_{\nu''}dr. \tag{C20}$$

Therefore

$$t_{kk'}=d_kd_{k'}\sum_{\nu''}\frac{(k|\nu'')(\nu''|k')}{z-\epsilon_{\nu''}}-d_k\delta_{kk'}. \tag{C21}$$

Now in general the spectrum of h will consist of two parts: a set of bound states $\epsilon_b(<0)$, and a quasi-continuous spectrum (continuous in the limit of an infinite volume) $\epsilon_\sigma(\geq 0)$. Thus we may write (C21) as

$$t_{kk'}=d_k\cdot d_{k'}\left[\sum_b\frac{(k|b)(b|k')}{z-\epsilon_b}+\sum_\sigma\frac{(k|\sigma)(\sigma|k')}{z-\epsilon_\sigma}\right]-d_k\delta_{kk'}. \tag{C22}$$

Therefore $t_{kk'}$ has *simple poles* at $z=\epsilon_b$. The residues at these poles are

$$\begin{aligned}r_{kk'}{}^{(b)}&=[d_kd_{k'}(k|b)(b|k')]_{z=\epsilon_b}\\ &=(\epsilon_b-\epsilon_k)(\epsilon_b-\epsilon_{k'})(k|b)(b|k').\end{aligned} \tag{C23}$$

The contribution to $t_{kk'}$ from the "continuum" ϵ_σ has a more complicated analytical behavior. If, however, we assume that the transformation coefficients $(k|\sigma)$ are smooth functions of the energy (they will depend in general on other parameters as well) then in the limit of infinite volume the sum over σ may be replaced by an integral. It is clear that as long as z is not on the positive real axis the denominator never can vanish, so that this contribution to $t_{kk'}$ is perfectly regular. Right on the positive real axis (C22) has no meaning. Immediately above the positive real axis we have $z=E+i\eta(\eta\to 0^+)$. Then

$$\frac{1}{z-\epsilon_\sigma}=\frac{1}{E-\epsilon_\sigma+i\eta}\to P\left(\frac{1}{E-\epsilon_\sigma}\right)-i\pi\delta(E-\epsilon_\sigma), \tag{C24}$$

so that (C22) takes on a definite value there. Immediately below, $z=E-i\eta$ and

$$\frac{1}{z-\epsilon_\sigma}=\frac{1}{E-\epsilon_\sigma-i\eta}\to P\left(\frac{1}{E-\epsilon_\sigma}\right)+i\pi\delta(E-\epsilon_\sigma). \tag{C25}$$

Therefore $t_{kk'}(z)$ changes its value abruptly as we cross the positive real axis but is analytic everywhere else in the finite z plane (except at the simple poles ϵ_b). In the limit of infinite volume $t_{kk'}(z)$ has a *branch line* along the positive real axis.

We also need the behavior of t for very large $|z|$. This is found by iterating (C5):

$$\begin{aligned}t&=\varphi+\frac{1}{d}\varphi+\frac{1}{d}\frac{1}{d}\varphi+\cdots,\\ t_{kk'}&=\varphi_{kk'}+\sum_{k''}\frac{\varphi_{kk''}\varphi_{k''k'}}{z-\epsilon_{k''}}+\cdots.\end{aligned} \tag{C26}$$

For fixed k and k' and localized scattering centers $\varphi_{kk''}\varphi_{k''k'}$ will decrease rapidly as $|k''|$ increases and the summation will converge long before $\epsilon_{k''}$ is comparable with $|z|$. Therefore for large $|z|$ we have

$$\begin{aligned}t_{kk'}(z)&=\varphi_{kk''}+\frac{\sum_{k''}\varphi_{kk''}\varphi_{k''k'}}{z}+\cdots\\ &=\varphi_{kk'}+\frac{(\varphi^2)_{kk'}}{z}+\cdots.\end{aligned} \tag{C27}$$

That is, for large $|z|$ and fixed k, k', $t_{kk'}(z)$ is simply a constant.

The analyticity arguments given here are admittedly heuristic. For the case of a one-dimensional δ-function potential, we have explicitly verified the above mentioned analytical properties of t. A more complete treatment is beyond the scope of this paper, however. The interested reader is referred to our colleague R. Jost.

We conclude this appendix with the generalization of the usual Optical Theorem which we shall need. If we apply (59) to the case of a single scatterer located at the origin, we obtain

$$0=\frac{2\epsilon^2}{\pi}\int_{-\infty}^{\infty}\frac{dE}{|d_k{}^+|^2}\left\{\frac{t_{kk}{}^+}{d_k{}^+}+\frac{t_{kk}{}^-}{d_k{}^-}+\sum_{k'}\frac{|t_{kk'}{}^+|^2}{|d_{k'}{}^+|^2}\right\} \tag{C28}$$

$$=i[t_{kk}(\epsilon_k-is)-t_{kk}(\epsilon_k+is)]+\sum_{k'}\sigma_{kk'} \tag{C29}$$

on evaluating the first two integrals and using (91).

As s approaches zero, this becomes, on using (101),

$$0=i[t_{kk}(\epsilon_k{}^-)-t_{kk}(\epsilon_k{}^+)]+\sum_{k'}w_{kk'}. \tag{C30}$$

We may write (C30) as

$$2\ \mathrm{Im}[t_{kk}(\epsilon_k{}^-)]=\sum_{k'}w_{kk'}, \tag{C31}$$

which is the usual Optical Theorem.

We need the correction to this of order s, which is

$$i(t_{kk}^{-}(\epsilon_k)-t_{kk}^{+}(\epsilon_k))$$
$$+\epsilon\left[\frac{\partial[t_{kk}^{+}(E)+t_{kk}^{-}(E)]}{\partial E}\right]_{E=\epsilon_k}+\sum_{k'}\sigma_{kk'}=0. \quad \text{(C32)}$$

From (134) this may be written

$$2r_k(\epsilon_k)=\sum_{k'}\sigma_{kk'}+s\left[\frac{\partial\Delta_k(E)}{\partial E}\right]_{\epsilon=\epsilon_k}. \quad \text{(C33)}$$

If we had started the derivation with the identity

$$1=-\frac{\epsilon}{\pi}\int_{-\infty}^{\infty}R^{-}R^{+}dE, \quad \text{(C34)}$$

then one could easily see that

$$2r_k(\epsilon_k)=\sum_{k'}\sigma_{k'k}+s\left[\frac{\partial\Delta_k(E)}{\partial E}\right]_{\epsilon_k} \quad \text{(C35)}$$

replaces (C33). Therefore we have

$$\sum_k\sigma_{kk'}=\sum_k\sigma_{k'k}, \quad \text{(C36)}$$

which becomes for $s\rightarrow 0$

$$\sum_{k'}w_{kk'}=\sum_{k'}w_{k'k}, \quad \text{(C37)}$$

a well-known identity.

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Semiconducting Properties of Mg_2Si Single Crystals*†

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High-purity n-type single crystals of the semiconducting compound Mg_2Si were prepared from melts of stoichiometric proportions of the constituents in graphite crucibles; p-type crystals were obtained when the melt was doped with silver or copper. Carrier concentrations in the saturation region were as low as 8×10^{16} cm^{-3} for n-type and 4×10^{17} cm^{-3} for p-type samples. Electrical resistivity ρ and Hall coefficient R were measured from 77°K to 1000°K. Hall mobility R/ρ showed a temperature dependence in the intrinsic range of approximately $T^{-\frac{3}{2}}$ for all samples. At 300°K, R/ρ was as high as 406 cm^2/volt-sec for n-type and 56 cm^2/volt-sec for p-type material. The ratio of electron mobility to hole mobility was approximately five. The energy gap, determined from the least-square slopes at high temperature of the curves $\log(RT^{\frac{3}{2}})$ *vs* $1/T$, was 0.78 ev. The electron mobility at any temperature in the range 77° to 400°K can be explained quantitatively by a combination of scattering by optical modes and scattering by ionized impurities.

INTRODUCTION

THE compounds Mg_2X, where X is silicon, germanium, or tin, are semiconductors having the antifluorite structure. Single crystals of n-type and p-type Mg_2Sn have been studied by Blunt *et al.*[1] Winkler[2] has investigated polycrystalline Mg_2Sn, Mg_2Ge, and Mg_2Si and Whitsett and Danielson[3] and Nelson[4] have studied single crystals of n-type Mg_2Si. A complete analysis of Hall and resistivity data requires both n-type and p-type material, and measurements on single crystals are more likely to yield carrier mobilities unobscured by the effects of grain boundaries, eutectic inclusions, and dislocations. The present paper reports results of resistivity and Hall effect measurements on high-purity n-type and p-type Mg_2Si single crystals.[5] The following paper[6] reports results for Mg_2Ge.

PREPARATION OF SAMPLES

Sublimed magnesium with a purity of 99.99% or higher, supplied by Dow Chemical Company, and Sylvania transistor-grade silicon were used to prepare Mg_2Si single crystals. Stoichiometric proportions of Mg and Si were melted together in a graphite crucible with a spectrographically-pure graphite liner 6.4 cm long and 1.6 cm in inside diameter. Thermocouples were placed in the crucible wall near the top and bottom

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[1] Blunt, Frederikse, and Hosler, Phys. Rev. **100**, 663 (1955).
[2] U. Winkler, Helv. Phys. Acta **28**, 633 (1955).
[3] C. R. Whitsett and G. C. Danielson, Phys. Rev. **100**, 1261(A) (1955).
[4] J. T. Nelson, Am. J. Phys. **23**, 390(A) (1955).
[5] R. G. Morris, Ph.D. thesis, Iowa State College, 1957 (unpublished). Preliminary results appear in Bull. Am. Phys. Soc. Ser. II, **2**, 120 (1957).
[6] Redin, Morris, and Danielson, Phys. Rev. **109**, 1916 (1957), following paper.